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DEPARTMENT OF COMMERCE

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 25

**STANDARD ANALYZED SAMPLES—
GENERAL INFORMATION**

[5th Edition]

Issued September 1, 1913



WASHINGTON
GOVERNMENT PRINTING OFFICE
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CONTENTS

	Page
I. Introduction	3
II. Function of standard analyzed samples	4
III. History of Bureau of Standards' samples	4
American Foundrymen's Association samples—American Chemical Society sam- ples—Other Bureau of Standards' samples.	
IV. The choice of standard materials:	
1. Metals—Similarity between standards and technical materials—Homogeneity of materials	5
2. Ores and similar materials—Hygroscopic qualities	6
V. Preparation of materials:	
1. Metals—Steel, iron, and brass	6
2. Difficulties encountered in renewal of metal samples—Proper composition— Homogeneity—Mixing	7
3. Ores, etc., grinding and mixing	7
4. Pure chemicals—Sugar—Naphthalene—Benzoic Acid—Sodium oxalate	8
VI. Uses of the standard samples	10
Settling disputes—Standardizing solutions—Testing new methods—Practice materials—Calibration of physical apparatus.	
VII. General considerations	10
Cooperation of journals and societies in past and future work.	
VIII. Standard analyzed samples issued or in preparation	11
IX. Ordering and shipping regulations	11
Ordering—Terms—Discount—Shipping—Samples out of stock—New samples— Mixing.	

I. INTRODUCTION

In the past fifteen or twenty years analytical chemistry has taken a place of such importance in many manufacturing industries that not only is the analyst called upon to determine the policy of the works in buying raw material and in grading finished products, but often his figures are required at every step of the process. This has necessitated many changes and advances in this science, for on the one hand the great complexity of many industrial products from a chemical point of view has increased the difficulty of securing good determinations, and on the other hand it has been necessary to obtain results much more promptly than heretofore.

II. FUNCTION OF STANDARD ANALYZED SAMPLES

The variable factors in analytical chemistry are many. The purity of reagents used, the influence of other elements on the determination of a particular element, the influence of temperature, changes of concentration, solubility of precipitates, catalytic phenomena, recognized and unrecognized, solubility of glass vessels, etc., these are but a few of the long list with which the chemist has to contend. It is obvious that the technical chemist when called upon to devise new and rapid methods to fit complex materials of a hitherto uninvestigated nature can not generally avail himself of the methods of the research chemist in handling but one or two of these variables at a time. The time at his disposal for investigation is necessarily limited and research must be conducted along lines of greatest efficiency. The result has been the evolution of the standard or analyzed sample. This may be defined as a material resembling as closely as possible the chemical and physical nature of the material with which the chemist expects to deal, and which has been analyzed by a sufficient number of methods and analysts to establish its average composition with considerable certainty. The use of such a sample is quite obvious where the chemist has at hand a material which when subjected to the usual operation of analysis will behave like the stock material he expects to analyze. Errors arising from solubility of precipitates, varying concentrations, effects of one element upon the precipitation of another, etc., will affect both sample and standard alike. Hence, if standard and sample are analyzed at the same time (and under practically identical conditions) and results are obtained for the standard corresponding to those obtained by the other analysts, the presumption is strong that the figures obtained for the unknown material are equally accurate, whereas wide divergence from the determinations made by the other chemists on the standard sample shows at once something radically wrong, such as improper method, personal equation, or faulty reagents. Thus in the simplest possible manner and in the shortest possible time a large number of variable factors have been simultaneously investigated with almost the same result as though each had been taken up separately.

III. HISTORY OF THE BUREAU OF STANDARDS' SAMPLES

When the chemical division of the Bureau of Standards was organized it was but natural that it should sooner or later be confronted with this requirement of the industries of the country. In 1905 the American Foundrymen's Association turned over to the Bureau its standardized pig-iron samples, comprising four sets and covering a considerable range of compositions. The distribution of these was carried on after they had been reanalyzed by the Bureau chemists and by some commercial testing laboratories. The Bureau, however, had not participated long as a distributor of these irons before it was recognized from the numerous inquiries received that

the preparation of new materials for the steel trade was in order, and consequently, aided by valuable suggestions and advice from various steel companies and from A. L. Colby, at that time a member of the visiting committee of the Bureau, and others, the issuing of various kinds of steel samples was begun and is being actively continued at the present time. In 1905 the committees of the American Chemical Society upon uniformity of technical analysis, and upon zinc ore analysis, assigned their samples to the Bureau of Standards for distribution. Along with the demand for steel and iron products there has developed demand for other alloys, for ores, and numerous other products, which is also being met as fast as the facilities of the Bureau permit.

IV. THE CHOICE OF STANDARD MATERIALS

1. METALS

Theoretically there should be provided for the chemist at a works as many standard samples as he has different kinds of materials to deal with. Thus, in a steel works making steel by the Bessemer, basic open-hearth, and crucible processes, in addition to standards for all the raw materials, there should be as many steel standards as there are processes, and a standard sample for each different composition produced by the same process if there is much range. Sometimes, however, there need not be absolute similarity in all respects between the product and standard; for instance, sometimes a steel sample is ordered on the basis of its carbon content without very much regard to the percentage of phosphorus present. This is a matter that must be determined, however, for each individual case and no general rule can be given. The Bureau in determining the question as to composition of samples to be issued is guided by the number and kind of requests received and by the advice of those engaged in the industries interested.

Metal samples should be in grains of small and uniform size, such that attack by chemical reagents is comparatively rapid; the size and the heat treatment must be such as to produce this result. It is especially important to have uniformity of size and freedom from dust, for it is only in this way that it is possible to obtain and maintain a perfect mixture. The works in preparing raw materials for analyzed samples must see that they possess extraordinary homogeneity. This is secured by forging, heat treatment, rolling, etc., under expert supervision. In general, the greatest homogeneity is possible with metals whose constituents form solid solutions. Wherever eutectics separate there is danger of segregation, which can only be avoided by the greatest care throughout subsequent operations. In the course of preparing the chips by machining of various kinds the particles of the sample must not be heated by the tool so much as to cause superficial oxidation, nor must they be exposed to the danger of corrosion by moist air after their preparation.

2. ORES AND SIMILAR MATERIALS

The ideal ore sample is one which is practically a chemically pure compound of the type which is being smelted, usually an oxide or a sulphide. Frequently ores are found in nature which satisfy this condition. If an ore sample is a blend the difficulty of uniform mixing is a prominent one, and where it is a question of the most thorough mixing of 200 or 300 pounds of such a blend under conditions of chemically pure cleanliness the problem is very complex. Another desirable quality in an ore is permanency with regard to its hygroscopic condition, the hardest of all to meet. In the case of ores containing 60 or 70 per cent of the metal which is to be recovered by smelting, differences of a few tenths of a per cent moisture make very considerable differences in the determination of the metal. A fine state of division is even more important here than in the case of metals, owing to the oftentimes difficult solubility, but this is incompatible in many cases with the desired hygroscopic qualities, for the readiness with which moisture is taken up by powdered materials is a function of their fineness.

V. PREPARATION OF MATERIALS

1. METALS

The raw material for the steel samples is supplied in the form of round bars about 5 inches in diameter, which have been carefully rolled or forged. These are cut into convenient lengths in the shop and, in order to see if they are sufficiently homogeneous, cuts are taken on the lathe to different depths and analyzed for carbon. If these preliminary tests show the bars to be sufficiently uniform they are turned into chips of the desired form. The amount of sample prepared in the past has ranged from 200 to 300 pounds. Sometimes it is not possible to produce directly on the lathe exactly the form of chip desired, and it then becomes necessary to grind the material in order to break up clumps of chips. The process of preparing the metals as outlined is somewhat wasteful both of time and material, but so far as steel is concerned it seems the only practicable one at present. Of course, in the preparation of these samples it is necessary to take the utmost precautions to prevent contamination by oil, dust, etc., and the storage of the finished samples requires similar precautions.

One of the brass samples has been prepared by clamping together in a vise a number of sheets of the material, of average thickness about one one-hundredth of an inch, and cutting chips from these with a milling cutter. This method can not be employed for steel and iron samples, owing to the oxidation of the surfaces of rolled sheets.

Pig-iron samples are not very difficult to prepare. Chips are cut from hollow cylinders 20 inches in diameter, with walls about 2 inches thick, which have been cast according to methods devised by the American Foundrymen's Association with a view to preventing segregation. The

greatest difficulty experienced here is the separation of graphite, which can not be kept uniformly mixed with the metal particles. In the samples prepared at the Bureau this difficulty has been overcome by blowing a strong current of air through the material, which is caused to fall in a thin layer at right angles to the air current.

2. DIFFICULTIES ENCOUNTERED IN RENEWAL OF METAL SAMPLES

As said before, the iron samples were originally obtained by transfer from the American Foundrymen's Association. As these approached exhaustion, efforts were made to replace them through the original source, but without success. It should be said that this failure was due to no lack of interest on the part of those who had originally prepared the castings. It was long before the Bureau was able to make arrangements for procuring and mixing materials that would afford a product sufficiently near the originals in composition, and for casting this product under such expert supervision as to insure a proper degree of homogeneity.

To insufficient experience on the part of the Bureau and the foundry undertaking the casting may, perhaps, be due the inhomogeneity that manifested itself in one of the iron samples thus prepared. This defect as shown by analysis was so great, notwithstanding careful sifting and long mixing, that the whole operation had to be repeated.

3. ORES, ETC., GRINDING AND MIXING

Ores and similar materials are prepared with comparative ease by grinding in a pebble mill lined with enameled brick and supplied with flint or porcelain pebbles.

With such mills a subsequent sifting of the powder is imperative, for the balls chip (particularly those of flint), and the chips produced in the later stage of grinding are not reduced to powder. In general the grinding of ores in contact with iron or steel surfaces is objectionable, sometimes quite inadmissible, for it always results in the incorporation of considerable amounts of metallic particles with the sample, and these are especially objectionable in that they are never uniformly distributed. Unfortunately the sifting above referred to occasions more or less segregation, hence thorough remixing must supervene under conditions that will permit no entrance of foreign matter. This thorough mixing applies to irons and steels as well as to ores. A mixer, built of two hollow internally enameled, cast-iron cones, bolted together at their bases and turning about a hollow axle at right-angles to their common axis, has been devised at the Bureau and is used for mixing metal samples. A blast of air may be directed through the axle, if desired.

The mixed samples are transferred to numbered Mason jars (glass) and from these to the small bottles in which they are to be finally distributed.

In order to expedite the process of transferring the finished material to the sample bottles, an apparatus has been devised whereby automatic delivery of any determined weight is made into the bottle through a funnel. The outlet of the latter is closed electrically the moment the required amount has passed.

But before the final bottling samples for analysis are removed from the jars and sent, one each, to a number of analysts. Each sample sent bears the number of the jar from which it was taken. In general three types of analysts are chosen—commercial chemists, works chemists, and chemists of the Bureau. When all the analytical results have been received they are inspected and, if not sufficiently concordant, analysts are sometimes requested to repeat the determinations without knowing the direction from the mean in which their value lies.

4. PURE CHEMICALS

In the selection of pure chemicals which may serve as primary standards for various purposes the effort has been made to choose stable substances, of the highest purity that can be obtained at reasonable expense. Where products of the requisite purity can not be obtained from the manufacturers, methods and apparatus for effecting the purification on a semi-industrial scale have been developed at this Bureau. So far as possible, the impurities in the final products are reduced to such an amount as to be outside the present limits of experimental error of the method which it is intended to standardize; i. e., the materials may be considered entirely pure for the purposes under consideration. In addition, however, careful tests are made to detect and if possible determine quantitatively any impurities present, in order that corrections may be made if necessary. Thus far the following samples have been issued:

Sugar.—Calorimetric and saccharimetric standard. The raw material for the standard sugar samples is drawn from the purest granulated sugar of commerce. A comparatively dilute solution is filtered and boiled in an improved vacuum apparatus to high concentration at temperatures below 35°C . Minute crystals form under the influence of constant stirring, which are separated by a powerful centrifugal machine. This process is repeated until analysis shows a negligible amount of ash and reducing substances. The final crystals are ground in an agate mortar and dried in a vacuum over lime. The substance is only slightly hygroscopic, but should be kept tightly stoppered in a dry compartment, at a temperature not much above 20°C , in order to prevent a slight spontaneous decomposition. Standard sugar samples prepared by a modified alcohol-precipitation method may also be obtained.

Naphthalene.—Calorimetric standard. The most common impurities in commercial naphthalene are sulphur compounds, which are eliminated with difficulty. The standard naphthalene samples are prepared from material

as free from sulphur as possible by two crystallizations from benzol, followed by one crystallization from alcohol and sublimation in vacuo. The purification is followed by determination of the sulphur content (which is below 0.05 per cent in the final product), the melting point and the calorific value. Naphthalene is not hygroscopic but is appreciably volatile, and care must be taken in accurate work to prevent error from the latter source.

Benzoic Acid.—Issued primarily as a calorimetric standard, but may be also employed in acidimetry. Benzoic acid as purchased in the open market may contain acid chlorides if made synthetically, or gums and related organic acids if made from natural sources. The standard samples are prepared from the purest synthetic benzoic acid obtainable, by two crystallizations from ethyl alcohol, followed by one crystallization from water and fractional sublimation in vacuo. The progress of purification is followed by titration with standard alkali, and the final product is tested for chlorine and sulphur, and the melting point and acid and calorimetric values are determined. Benzoic acid is neither appreciably volatile nor hygroscopic,¹ and when prepared as above and kept in stoppered bottles can be used for all but the most accurate work without preliminary drying.

For details regarding the use of combustion samples, consult Bureau of Standards Circular No. 11.

Sodium Oxalate.—Issued primarily as an oxidimetric standard, but may be used for acidimetry. This material was prepared, upon rigid specifications, by the Mallinckrodt Chemical Works, St. Louis, Mo., and was carefully tested at this Bureau. For details regarding the use of sodium oxalate, consult Bureau of Standards Circular No. 40 on "Sodium oxalate as a standard in volumetric analysis."

Dextrose.—Standard reducing sugar. High-grade glucose of commerce containing about 87 per cent of dextrose is washed with aqueous alcohol, dissolved in a small quantity of hot water and treated with alcohol to precipitate the dextrans. The filtered solution is boiled in a vacuum to a concentration of 60 per cent and finally rotated in a shaking machine for 24 hours to permit crystallization. The crystals are centrifuged and washed with alcohol. The entire process is repeated until a satisfactory purity is attained. The crystals obtained in this fashion contain one molecule of water of crystallization, but the substance loses this at 60° C, a temperature considerably below the melting point. The remaining traces of moisture are removed by exposing to a temperature of 80° to 100° in a vacuum over freshly ignited lime. The dried substance in spite of its finely divided condition is not very hygroscopic, but should be kept in a desiccator. If the sample for analysis is weighed in such manner as to avoid exposure to a damp atmosphere, the moisture content is less than 0.01 per cent.

¹ It has been found, however, to take up moisture from the air very slowly. Old samples may contain as much as 0.1 per cent of water, which can be easily removed by careful fusion. See forthcoming paper: "Note on the use of benzoic acid as a standard material," by E. R. Weaver, in J. Am. Chem. Soc.

VI. USES OF THE STANDARD SAMPLES

The principal uses of the Bureau's analyzed samples appear to be as follows **First:** In the settling and avoiding of disputes between buyers and sellers. Such disputes very frequently arise through the selection of inappropriate or faulty methods of analysis by one of the chemists, and the analysis of a standard material usually brings these to light before the case comes to court. **Second:** In standardizing volumetric solutions; for example, the determination of sulphur and manganese in iron and steel; iron ores are used for establishing the iron standard for permanganate or bichromate solutions, from which the standards for most other titrations are calculated. **Third:** As material for trying out new methods. The use in this connection is obvious. **Fourth:** As practice material for new and inexperienced chemists. They have quite an extended use in universities in this connection. **Fifth:** The combustion samples for standardizing calorimeters and the sugar for the same purpose as well as for polariscopes.

VII. GENERAL CONSIDERATIONS

In conclusion it may be said that the Bureau's work in providing analyzed samples has attracted considerable attention and interest, partly because of its intrinsic merit and partly because the Bureau has sought, through brief mention in the leading chemical and engineering journals of the country, to secure the attention and interest of those who need this kind of service. The result has been the hearty and oftentimes unsolicited cooperation of some of the leading testing societies of the country. Among these are the American Foundrymen's Association, the American Brass Founders' Association, the American Steel Manufacturers Association, the United States Steel Corporation, the American Chemical Society, and the American Society for Testing Materials. The latter society has recently organized two new committees—a committee on nonferrous alloys and a committee on alloy steels—on which the Bureau is represented. It will be one of the functions of these committees, which include in their personnel members of the technical staffs of some of the leading manufacturers of the country, to suggest some of the future lines of activity of the Bureau in the work it has begun on analyzed samples and to aid it in selecting and securing the necessary raw materials.

VIII. STANDARD ANALYZED SAMPLES ISSUED OR IN PREPARATION

The samples are numbered consecutively nearly in the order of issuance of the first representative of each kind. Renewals of a sample are indicated by the original number, with an added letter to denote its intended relation. Thus, 5a is the first renewal by the Bureau of Standards of the original Iron C. In this way a given number will always represent a material of fixed, or approximately fixed, composition. Numbers missing from the series in the table in the "Insert to accompany Bureau of Standards Circular No. 25" represent samples of which the supply has become exhausted, and which it is not the present intention to replace.

The sample numbers and their analyses in the "Insert" are subject to correction from time to time to take account of the somewhat different composition of each "Renewal" sample.

IX. ORDERING AND SHIPPING REGULATIONS

Ordering.—Orders should give both the number and name of the sample wanted. Example: No. 9a Steel, Bessemer 0.2 C. The list of standard samples, their numbers, prices, and analyses are to be found in the "Insert to accompany Bureau of Standards Circular No. 25."

Terms.—Prepayment in full is required by the regulations of this Department before samples can be shipped. Payment may be by check, draft, postal or express money order, and should be payable to the "Secretary of Commerce."

Discount.—Ten per cent discount is allowed on the list price when four or more samples (alike or different) are ordered at one time. No samples are distributed of smaller size than those listed.

Shipping.—Samples, if not numerous, are sent by mail under Government frank without expense to the purchaser, unless other instructions are given. If sent by express, it is at the expense of the purchaser.

Iron, steel, and ore samples are sent in screw-capped glass bottles, and organic samples in glass-stoppered bottles, under seal.

Detailed certificates of analysis, and also gummed labels with the summary of analysis, together with the corresponding descriptive circulars, are sent with samples. In the case of new or renewal samples, provisional typewritten certificates will be supplied until they can be replaced by the printed certificates and labels when ready.

Samples out of Stock.—The preparation of new or "Renewal" samples to replace exhausted stock is intended to be complete at the time each kind of sample becomes exhausted, but owing to delays encountered in securing a proper grade of material and for other reasons, this is not always possible. In case of orders for samples thus out of stock, but soon to be replaced, the fee covering the entire order will be charged unless other instructions are sent, and the "Renewal" sample will be sent when ready, without further

notice. Should a long delay be necessary, refund will be made, and notice mailed when the "Renewal" is ready. The "Renewal" will have a composition more or less different from that of its predecessor, but as regards the characteristic constituent or constituents will pattern after it closely.

New Samples.—When new samples are issued, announcement will be made in the following journals: Iron Age, Journal of Industrial and Engineering Chemistry, and Metallurgical and Chemical Engineer.

Mixing.—In order to overcome the effect of any segregation in shipment the contents of each bottle (except the organic samples) *should be thoroughly mixed before any is used for analysis.*

S. W. STRATTON,
Director.

Approved:

A. L. THURMAN,
Acting Secretary.



